
TOTAL OXIDATION OF METHANOL AT LOW TEMPERATURES ON (Cu, Mn)-Mg-Al MIXED METAL OXIDES DERIVED FROM HYDROTALCITES

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Abstract: A series of (Cu, Mn)-Mg-Al hydrotalcite-like layered double hydroxides (HTs) was synthesized by a co-precipitation method. The incorporation of Mn into the Mg-Al and Cu-Mg-Al HTs structure was investigated by employing powder X-ray diffraction. Calcination of the precursors resulted in destruction of the layered structure and led to low-crystalline MgO. Obtained mixed metal oxides were tested as catalysts for the process of total oxidation of methanol. The catalytic performance of the Cu-containing samples was better comparing to the Mn-based catalysts and decreased in the following order: Cu-Mg-Al > Cu-Mn-Mg-Al > Mn-Mg-Al > Mg-Al. Quantitative total oxidation of methanol was achieved at 325°C with Cu-Mg-Al mixed oxides.

1. Introduction

Hydrotalcite-like compounds are a group of naturally occurring anionic clays. The structure of these materials can be described with the general formula of $[M_{1-x}^{II}M_x^{III}(\text{OH})_2]^{x+}A_{x/z}^{z-} \cdot n\text{H}_2\text{O}$, where M^{II} and M^{III} are two- and trivalent cations, respectively, A - interlayer anions, while x is the molar ratio of the metal cations, whose value varies in the range of 0.15-0.34 (Cavani et al., 1991). It is possible to synthesize a broad variety of hydrotalcite-like materials containing different divalent (e.g. Mg^{2+} , Ni^{2+} , Zn^{2+} etc.) and trivalent cations (e.g. Al^{3+} , Fe^{3+} , Cr^{3+} etc.) as well as both organic or inorganic interlayer anions (e.g. CO_3^{2-} , $\text{Cr}_2\text{O}_7^{2-}$, $\text{Mo}_7\text{O}_{24}^{6-}$ etc.) (Millange et al., 2000; Valente et al., 2009). Hydrotalcite-like materials and mixed oxides obtained by their thermal decomposition have been used as active environmental catalysts (Chmielarz et al., 2002, 2011) and they can be an alternative catalysts for the total oxidation of mono-carbon VOCs (e.g. methane, methanol, and formic acid) (Chmielarz et al., 2012). Mn-containing oxides derived from hydrotalcite-like compounds have been widely studied as potential catalysts for total VOCs oxidation. For example, the successful use of Mg-Mn-(Al) mixed metal oxides obtained from

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hydrotalcite-like materials was reported in catalytic combustion of methane (Jiráťová et al., 2002) or toluene (Velu et al., 1999). On the contrary only few reports are related to the applications of Cu-based hydrotalcite-like derivatives. An example could be Cu-Mn-Al mixed metal oxide studied in the process of the total oxidation of toluene (Palacio et al., 2010; Zimowska et al., 2007). The temperature needed for 50% conversion of toluene to CO_2 was among the lowest reported in literature (Kovanda et al., 2001; Lamonier et al., 2007; Mikulová et al., 2007; Zimowska et al., 2007).

In the present study similar catalytic systems based on hydrotalcite-like materials are studied and its catalytic performance in the total oxidation of methanol is carried out. A series of Cu/Mn-containing LDHs was synthesized by a simple co-precipitation method, whereas the changes in the physicochemical properties were investigated employing XRD and BET techniques.

2. Experimental part

2.1. Samples preparation

The Mg-Al, Cu(Mn)-Mg-Al, Cu-Mn-Mg-Al hydrotalcite-like samples with the intended molar ratios of 71.0:29.0, 5.0:66.0:29.0 or 2.5:2.5:66.0:29.0 were synthesized by a co-precipitation method using 1 M aqueous solutions of the following metal nitrates: $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (Merck), $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (Lach-Ner), $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Sigma) and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Fluka). A solution of NaOH (POCH) was used as a precipitating agent. Solution of metal nitrates and NaOH were simultaneously added to a vigorously stirred solution containing a slight excess of Na_2CO_3 (POCH). The pH was maintained at 9.0 ± 0.2 the constant value (with the exception of Mg-Al and Cu-Mg-Al hydrotalcite-like materials, which were synthesized at $\text{pH} = 10.0 \pm 0.2$) by dropwise addition of 1 M NaOH solution. The obtained slurry was aged at 60°C for 1 h, filtered, washed with distilled water and dried at room temperature. Mn-containing hydrotalcite-like materials were synthesized with stirring under an argon atmosphere. The as-synthesized samples were calcined in static air at 600°C for 12 h. For catalytic experiments, a fraction of the catalysts with a particle size in the range of 0.160-0.315 mm was selected.

2.2. Samples characterization

The crystalline structure of the as-synthesized and calcined samples was analysed by means of an X-ray powder D2 Phaser diffractometer (Bruker) using $\text{Cu K}\alpha$ radiation ($\lambda = 1.54060 \text{ \AA}$, 30 kV, 10 mA). Cell parameters were calculated using a position of 110 reflection: ($a = 2(d_{110})$) and positions of basal reflections ($c = [3(d_{003}) + 6(d_{006})]/2$). The parameter a corresponds to the cation-cation distance within the brucite-like layer, whereas the parameter c is related to the thickness of the brucite-like layer and interlayer distance. Crystal sizes were calculated from the Scherrer equation $D = 0.89 \lambda / \beta \cos \theta$, where D is the crystallite size, λ - the X-ray wavelength, β - the line broadening and θ - the Bragg angle.

The specific area of the calcined hydrotalcite-like materials was determined by low-temperature (-196°C) N_2 sorption using Quantasorb Junior sorptometer (Ankersmit). Prior to nitrogen adsorption the samples were out gassed at 250°C for 2 h in a flow of N_2 ($1.92 \text{ cm}^3/\text{min}$). The measurements were performed in a flow of N_2 ($1.92 \text{ cm}^3/\text{min}$).



and He (16.88 cm³/min).

2.3. Catalytic studies

Calcined hydrotalcites were tested as catalysts of methanol incineration. The catalytic experiments were performed under atmospheric pressure in a fixed-bed flow microreactor system. The reactant concentrations were continuously measured using a quadruple mass spectrometer RGA 200 (PREVAC) connected directly to the reactor outlet. Prior to the catalytic test each sample of the catalyst (100 mg) was out gassed in a flow of synthetic air 500 °C for 30 min. The isothermal saturator with a constant flow of synthetic air was used for supplying of methanol into the reaction mixture. The composition of gas mixture at the reactor inlet was [CH₃OH] = 4.0 vol.%, [O₂] = 19.0 vol.% and [N₂] = 77.0 vol.%. The reaction was studied in the range from 100 to 500 °C with the linear temperature increase of 10 °C/min. Total flow rate of the reaction mixture was 20 cm³/min.

3. Results and discussion

3.1. Powder X-ray diffraction

Powder XRD diffraction pattern obtained for the as-synthesized hydrotalcite-like materials and their derivatives are presented in Fig. 1. The obtained precursors exhibit a typical crystalline hydrotalcite-like structure belonging to the space group R3m in the trigonal symmetry (Węgrzyn et al., 2010). Cell parameters and crystallites sizes of the hydrotalcite-like samples, determined from XRD measurements, are presented in Tab. 1. The cell parameter *c* for all precursors obtained in the study of about 2.3 nm is typical for hydrotalcites containing carbonate as the interlayer anion (Chmielarz et al., 2011). XRD patterns of the calcined samples contain only the typical pattern of the poorly crystallized MgO-type mixed oxides (reflections at 36 °, 43 ° and 63 °) (Cavani et al., 1991).

Tab. 1. Structural parameters of hydrotalcite-like precursors

Sample codes	PFWHM of (003) peak (2 θ)	Cell parameter <i>a</i> [nm]	Crystallite size <i>D_a</i> [nm]	Cell parameter <i>c</i> [nm]	Crystallite size <i>D_c</i> [nm]
Mg-Al	1.1106	0.3046	24	2.2888	15
Cu-Mg-Al	1.1142	0.3050	26	2.2868	15
Cu-Mn-Mg-Al	1.6237	0.3054	26	2.3155	13
Mn-Mg-Al	1.3920	0.3062	29	2.3121	15

3.2. Specific surface area measurements

The specific surface area (*S_{BET}*) of the calcined samples are shown in Tab. 2. Specific surface area of the samples depends on their chemical composition. It should be noted



that incorporation of copper and/or manganese into the hydrotalcite-like framework, reduces their surface area comparing to the calcined Mg-Al sample.

Tab. 2. BET surface area of the calcined samples

Sample codes	BET surface area [m ² /g]
Mg-Al-600	173
Cu-Mg-Al-600	121
Cu-Mn-Mg-Al-600	118
Mn-Mg-Al-600	150

3.3. Catalytic activities

Calcined hydrotalcites were tested as catalysts for the complete oxidation of methanol. Carbon dioxide and water vapour were the only detected reaction products of methanol oxidation. Tab. 3 presents the results of methanol incineration. The activities of the catalysts are frequently characterized by two parameters, T_{50} and T_{90} . T_{50} refers to the temperature needed to reach 50% conversion, and is widely used to compare catalytic activity, while T_{90} is the temperature necessary for 90% conversion of methanol.

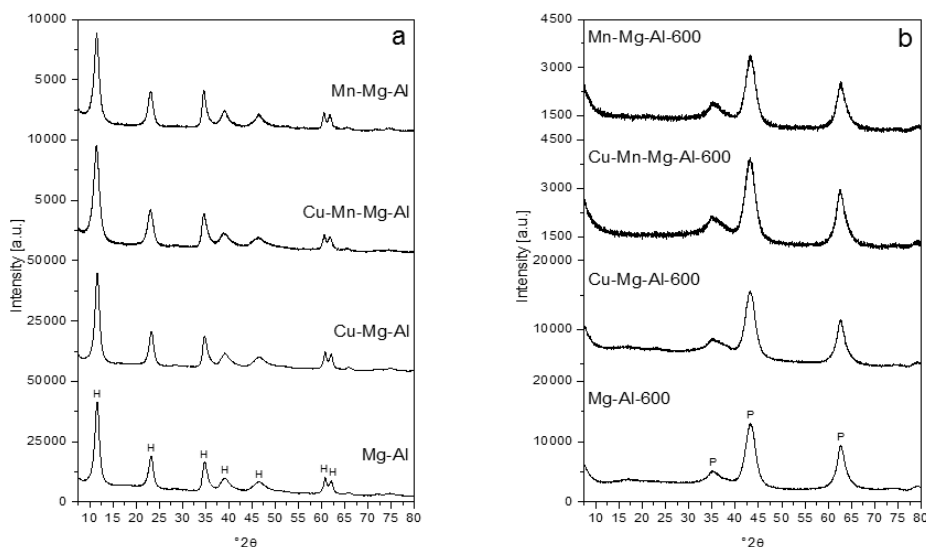


Fig. 1. X-ray diffraction patterns of (a) hydrotalcite-like precursors: Mg-Al, Cu-Mg-Al, Cu-Mn-Mg-Al, Mn-Mg-Al, (b) calcined materials: Mg-Al-600, Cu-Mg-Al-600, Cu-Mn-Mg-Al-600, Mn-Mg-Al-600; H – hydrotalcite-like materials, P – periclase (MgO)



Tab. 3. T_{50} and T_{90} temperatures of methanol oxidation over (Cu, Mn)-Mg-Al catalysts

Sample codes	$T_{50}/^{\circ}\text{C}$	$T_{90}/^{\circ}\text{C}$
Mg-Al-600	346	396
Cu-Mg-Al-600	252	281
Cu-Mn-Mg-Al-600	285	319
Mn-Mg-Al-600	302	340

Among all the studied catalysts, Cu-Mg-Al mixed oxides showed superior catalytic performance over the others both at T_{50} and T_{90} . The oxidation of methanol over these catalysts started at about 225°C , while its complete oxidation was possible at 325°C . The Mn-Mg-Al and Mg-Al mixed oxides were the least active catalyst in a studied series.

4. Conclusion

Mg-Al, Cu-Mg-Al, Cu-Mn-Mg-Al and Mn-Mg-Al hydrotalcite-like materials were successfully synthesized, what was confirmed by the results of powder X-ray diffraction studies. Calcination of the precursors at 600°C resulted in destruction of the layered structure and led to the formation of mixed metal oxides. Specific surface area strongly depended on the composition of the sample and decreased after introduction of transition metal into the Mg-Al structure. Activity of the catalysts in the reaction of complete oxidation of methanol strongly depended on the kind of transition metal introduced to the mixed oxides system. The Cu-containing catalysts were found to be active catalysts for total methanol oxidation. Further studies using different copper concentration, different calcination temperature and doping the material with some alkali or noble metals focused on the improvement of the catalytic activity of the studied samples are planned.

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